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## Fractal Geometry and Brownian Motion: A New Parameter to Describe Molecular Motion

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The lengths of molecular trajectories in an argonlike liquid simulated by molecular dynamics have been found to be fractal over a substantial range of scales with a Richardson coefficient of  $\alpha = 0.65$  (Mandelbrot dimensionality of  $d = 1.65$ ). The results obey a simple empirical relation with three parameters. We believe  $\alpha$  to be a useful new parameter to describe the form of trajectories of molecules in fluids where none has previously been available, and that it is a state function.

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The idea of fractional dimensionality goes back at least to Hausdorff.<sup>1</sup> It was in effect applied to the analysis of coastlines, etc., in a seminal paper by Richardson<sup>2</sup> and has recently been popularized by Mandelbrot's provocative book.<sup>3</sup> It is currently an attractive idea because it is a scaling phenomenon which may relate to Widom's scaling hypothesis<sup>4</sup> and Wilson's renormalization group<sup>5</sup> which are finding wide application in theoretical physics. This has made respectable the use of nonintegral dimensionality<sup>6</sup> in physical science.

Mandelbrot<sup>3</sup> discusses the application of fractal geometry to Brownian motion and even devotes a whole chapter to this topic. However, the connection between his analysis of mathematical models and the Brownian motion of molecules in real or at least realistic liquids is not very clear.

It is not yet possible in an actual experiment to follow the trajectory of a molecule in a real liquid in detail. We therefore utilize a computer simulation of a "typical" liquid in circumstances in which it is

known that this is a realistic model of an actual liquid such as liquid argon. We give only a few parameters of the simulation since it is quite conventional.

The intermolecular potential chosen was a central pair-wise Lennard-Jones 12-6 interaction potential cut off at a distance  $r = 2.5\sigma$ , where  $\sigma$  is the length parameter in the potential and is effectively the diameter of the molecule. We used 108 molecules with cyclic boundary conditions, a reduced density,  $\rho\sigma^3 = 0.65$  ( $\rho$  is the number density), and a reduced temperature,  $kT/e = 0.93$  ( $e$  is the energy parameter in the Lennard-Jones potential; we reserve the usual symbol,  $\epsilon$ , for the scale, see below). This is a typical liquid state about halfway between the triple point and the critical point and moreover is on the coexistence line so that the pressure applied to the liquid is the vapor pressure.<sup>7</sup>

The time step was 0.1 Verlet units<sup>8</sup> which corresponds, for the parameters for liquid argon, to about  $10^{-14}$  s. In the simulation we ran for 600

steps for equilibration and then for 5000 steps, the latter being much longer than the characteristic time for changes in the particle velocity, about  $10^{-13}$  s in this case. We recorded the trajectory of a particular atom and analyzed it for possible fractal properties.

It will be recalled that a fractal curve has the property that if one measures its length,  $L(\epsilon)$ , using a scale, i.e., a step distance,  $\epsilon$ , then

$$L(\epsilon) \propto \epsilon^{-\alpha},$$

where  $\alpha$  is a constant, at least for a set of particular values of  $\epsilon$ .

We employ here Richardson's empirical notation since it is  $\alpha$  which is actually measured. Mandelbrot advocates that  $\alpha$  should be regarded as  $d - d_T$  where  $d$  is a fractal dimension and  $d_T$  is the topological dimension.  $d_T = 1$  for our trajectories so that  $d = 1 + \alpha$  here.

An example of a fractal curve is the Koch curve,  $K_\infty$ , illustrated in Fig. 1, which we shall use later. For  $K_\infty$ ,

$$\alpha = (\ln 4 / \ln 3) - 1 = 0.2618 \dots,$$

provided  $\epsilon = 1/3^m$ , where 1 is the end-to-end length and  $m$  is an integer.  $K_\infty$  is a continuous nondifferentiable curve of infinite length, as is the quantum path of a particle.<sup>9</sup> In this paper, however, we consider only classical mechanics.

We proceed to analyze the molecular trajectory, after of course compensating for the discontinuities which arise from the use of cyclic boundary conditions. This "stretching" procedure is familiar to us in the determination of the self-diffusion coefficient,  $D$ , from a simulation. Since the trajectory is presumably continuous we regard  $\epsilon$  as a continuous variable as is  $L(\epsilon)$ . However, we present the

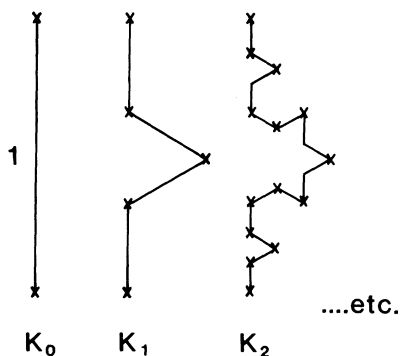


FIG. 1. The fractal Koch curves for which  $L(\epsilon/3) = (4/3)L(\epsilon)$  for  $\epsilon/1 = 1/3^m$ .  $\alpha = (\ln 4 / \ln 3) - 1$ , i.e.,  $d = 1.2618 \dots$

results in the manner of experimental results, in equal increments of  $-\log_2(\epsilon/\sigma)$ , which is convenient and appropriate. We have a program which measures  $L(\epsilon/\sigma)$  for any value of  $\epsilon$  by stepping along the trajectory as if with a pair of dividers. We take the trajectory between simulation time steps as straight lines but our time step is so short that this is entirely justified (see Fig. 2). We include end corrections which are fractions of  $\epsilon$  as recommended by Richardson.<sup>2</sup>

The result is shown in Fig. 2. For a large range of  $\epsilon$ , about  $2^4$ , we get a quite good straight line with a slope corresponding to  $\alpha = 0.65$ . For large values of  $\epsilon$  (note that  $\epsilon$  decreases to the right in the figures) we get the end-to-end distance,  $L_e$ , which on the average will be near the root mean square distance

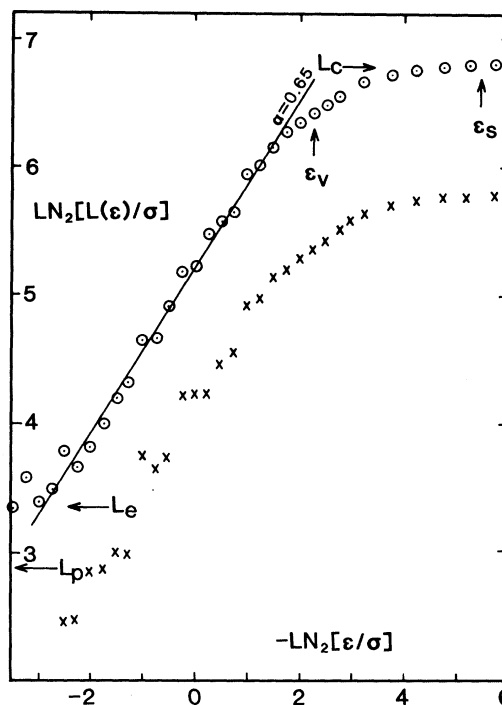


FIG. 2. Fractal analysis of the trajectory of a molecule in a typical liquid, from a computer simulation, circles.  $L(\epsilon/\sigma)$  is the length measured by stepping along the trajectory with "dividers" set at  $\epsilon/\sigma$ . Note:  $\epsilon/\sigma$  diminishes from left to right by a factor 2 for each unit.  $L_e$  is the observed end-to-end distance whose root mean square average over many trajectories would be  $L_r$ . The mean contour length,  $\langle L_c \rangle$ , depends only on the temperature. Also indicated is the mean value of  $\epsilon$  for one step of the simulation,  $\epsilon_s$ , and also the mean distance travelled for loss of correlation of the particle velocity,  $\epsilon_v$ . For a gas the latter would be the mean free path. The best straight line through the quasilinear part of the plot yields a value of Richardson's parameter of  $\alpha = 0.65$ . Also given is the corresponding plot of the first half of the same trajectory.

between the two ends of the trajectory,  $L_r$ , which, for these relatively long trajectories, is simply

$$L_r = (6DN\Delta t)^{1/2}.$$

We have measured the diffusion constant,  $D$ , although in fact Verlet's empirical formula<sup>8</sup> is quite adequate. For various particles and different trajectories (see below) there is of course a considerable statistical fluctuation of  $L_e$  about  $L_r$ .

For  $\epsilon$  small enough  $L(\epsilon)$  approaches the contour length,  $L_c$ . This is immediately estimated from

$$\langle L_c \rangle = \langle v \rangle N\Delta t,$$

where  $\langle v \rangle$  is the mean molecular speed which is determined by the temperature and the mass of the molecule. In reduced units it is independent of the mass of the molecule. Of course the actual contour length for any particular trajectory,  $L_c$ , fluctuates about the mean value but the fluctuations are relatively much smaller than for  $L_e$ .

Clearly the trajectory is not fractal for small enough  $\epsilon$ . It becomes effectively smooth, however, well before  $\epsilon$  is the mean step length of the simulation,  $\epsilon_s$ ; see Fig. 2. We have verified that the trajectory really is smooth because the plot in Fig. 2 is not affected if we use a computational step length one half as long or if we use only alternate points of the original trajectory.

We can guess that the scale at which the trajectory

starts to be appreciably smooth is given by

$$\epsilon_v \approx \langle v \rangle \tau_v,$$

where  $\tau_v$  is the correlation time of the molecular velocity.  $\tau_v$  is immediately obtained from  $D$  since  $\tau_v = (m/kT)D$ . This scale is marked in Fig. 2 and is, as expected, at the knee of the curve. For a gas  $\epsilon_v$  is virtually the mean free path.

We find that the curve in Fig. 2 is given with remarkable accuracy by the empirical relation

$$L(\epsilon) - L_c (\epsilon^2/\epsilon_v^2 + 1)^{-\alpha/2}.$$

We have also analyzed shorter trajectories for the same thermodynamic state, in fact parts of the trajectory used for Fig. 2. For the trajectories for steps 1-2500 (see Fig. 2), 2501-5000, 1-1250, 1251-2500, etc., the plots are indistinguishable from that in Fig. 2, after a vertical shift to compensate for the change in  $L_c$ . For the trajectories 1-625, etc., the plots are quite noisy and begin to diverge from Fig. 2. In any case such plots are clearly too short. The "gap" between  $L_c$  and  $L_r$  falls as  $N^{1/2}$ .

It appears therefore that the fractal coefficient,  $\alpha$ , and the form of the curve given above are independent of the trajectory length as long as one can reasonably make a plot such as Fig. 2. Only two parameters are required given the form above and the temperature: the self-diffusion constant which is trivial, and the fractal coefficient,  $\alpha$ . Thus  $\alpha$  is a

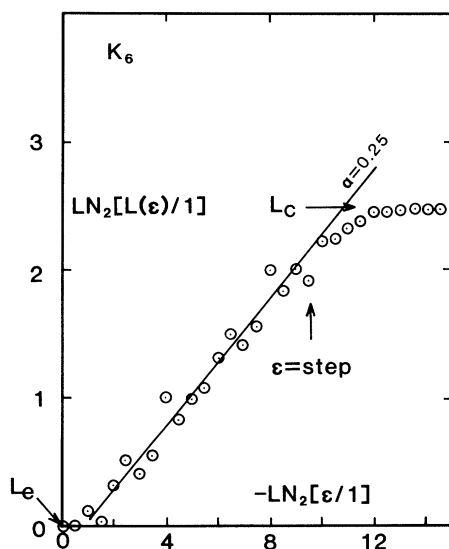


FIG. 3. A randomized Koch curve of order 6 analyzed as if it were a molecular trajectory. The apparent value of  $\alpha$  is 0.25 whereas for  $K_\infty$  it is 0.26... provided  $\epsilon/1 = 1/3^m$ . Compare with Fig. 2, but note the change of scale of abscissae.

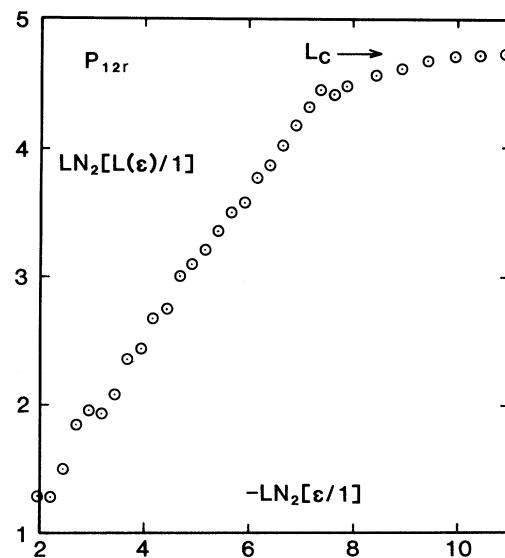


FIG. 4. Analysis of a randomized Peano curve of order 12 with  $\theta = 99.1135^\circ$  for which  $\alpha = 0.65$ . This curve, after translation of the axes, can be superimposed on the curve of Fig. 2.

new parameter for describing molecular motion in a liquid.

Mandelbrot<sup>3</sup> states (p. 15) that for Brownian motion,  $d=2$ , i.e.,  $\alpha=1$ , which is clearly not the case here. For reasons obscure to us he uses the model of the Peano curve (see below) with  $\theta$  having the critical value  $90^\circ$ . However, our results suggest that molecular trajectories undergoing Brownian motion are fractal to finite order, in the sense that at small enough scale they become smooth curves, as surely must be the case if we believe in Newton's law of motion.

In view of Mandelbrot's strong feelings about nomenclature we suggest with trepidation that our curves be called "finite fractals." In illustration of this point of view we have analyzed a Koch curve for  $n=6$ , i.e., 4096 steps, as if it were a molecular trajectory using our computer program just as we did for Fig. 2. The result is shown in Fig. 3. This bears a striking resemblance to Fig. 2. The best-fit line to the straight part gives  $\alpha=0.25$  which is within "experimental error" of the value, 0.262, which is for  $\epsilon/1=1/3^m$ . The exact result for any  $\epsilon$  is extremely complex so our result has "Laplacian" randomness. We have also randomized a  $K_6$  curve by placing the triangles to the left or right at random at each stage of development,  $K_1, K_2, \dots, K_6$ . The "experimental result" is then even more similar to that in Fig. 2. Indeed the curve itself is very similar to the real trajectory.

Finally, we have used as a finite fractal curve a randomized Peano curve of order 12 with  $\theta=99.1135^\circ$  (Fig. 4), which gives  $\alpha=0.65$ . The

shape of the analyzed curve is indistinguishable from that in Fig. 2 after suitable bodily translation which is permissible because of the arbitrariness of the scales. On the other hand the curve bears little apparent resemblance to the actual trajectory.

We have also looked at the trajectories of molecules in gases and crystals but we defer discussion of these to another place.

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